Global Solar Energy, Inc.
5575 South Houghton Road
Tucson, Arizona 85747
(520) 546-6313 (Voice)
(520) 546-6318 (FAX)

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Dr. Harin Ullal
Mail Stop 3212
National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401-3393

Re: Phase III, Second Quarterly Report #ZDJ-2-30630-14

Dear Harin,

This letter comprises the quarterly technical status report for Thin Film Partnership subcontract #ZDJ-2-30630-14. The reported work was performed during the second quarter of year 3 for this contract, from 8/15/04 to 11/15/04. This report describes activities performed by GSE, as well as those performed by lower-tier subcontractor ITN Energy Systems, Inc.

1. INTRODUCTION

Two-stage and three-stage CIGS coevaporation – followed by chemical bath CdS and RF-sputtered resistive and conductive ZnO – have come to be viewed as laboratory standards for the deposition of CIGS photovoltaic devices. However, a number of conditions are encountered during continuous manufacturing that prevent an exact replication of the laboratory processes. Such differences include both those imposed by continuous processing of moving substrates, and those implemented to decrease costs and increase throughput. It is, therefore, beneficial to understand the tolerance of the established laboratory processes to variations in deposition procedures.

Research under this program consists of four basic parts to examine the tolerance of the established laboratory process to variations in deposition procedures:

1. Setting up the National Renewable Energy Laboratory (NREL)-developed three-stage CIGS laboratory process in a bell jar.
2. Characterizing the GSE roll-to-roll production chambers and device finishing steps in terms of the variables important to the laboratory processes.
3. Using the bell jar system to step incrementally from the NREL process to the conditions experienced by a sample during manufacturing, and characterizing the resulting films and devices.

4. Applying the process sensitivity information gained from the bell jar system to the production systems.

Some portions of these tasks are being performed in parallel. At this time, items #1 and #2 are complete, and effort is focused on #3 and #4. This quarter, progress includes application of bell jar studies of Cu-rich growth to the production roll-coaters, evaluation of post-deposition treatments on production CIGS, documentation of the effect of source purity on device performance, work on decoupling substrate and CIGS growth effects through use of Al_2O_3 substrates, and examination of very fast depositions in the bell jar. These activities are described in more detail in the sections below.

2. MAXIMUM CU RATIO DURING CIGS GROWTH AND IMPLICATIONS FOR PRODUCTION

It was described in previous reports that, for three-stage devices made in ITN's bell jar, a Cu-rich growth period yields a statistically significant benefit on device performance. Experimental documentation of this benefit via experimental design will be presented at the upcoming IEEE PVSC meeting in January 2005.

Given the sensitivity of bell jar devices to maximum Cu ratio, tests of the impact of maximum Cu ratio were also performed in the GSE production roll-coaters. A two-level screening test of maximum and final Cu ratio was executed. The 2×2 matrix was replicated one time for a total of eight test conditions. The planned levels for Cu-rich excursion were 1.0 and 1.1, as measured by in-situ XRF. The planned levels for final composition (Cu/(Ga+In)) were 0.81 and 0.91. The web was processed according to baseline manufacturing process conditions through production cell (i.e., large area devices, total area 78 cm^2) fabrication and measurement. Three thirty-cell sample panels were extracted from each condition. Deletion of outliers well outside the normal distribution was performed prior to analysis.

The mean efficiency of each condition are plotted on the interaction chart in Figure 1. For films processed without a Cu-rich excursion (in process Cu/(Ga+In) ~ 1.0), the final composition had a significant effect on final efficiency; a final Cu/(Ga+In) of 0.91 was superior to 0.81. All IV parameters (V_{oc}, J_{sc}, and fill factor) improved. For films that experienced a Cu-rich excursion (in process Cu/(Ga+In) ~ 1.1), the efficiency was much less dependent on the final Cu/(Ga+In). The latter process was more robust, although the mean efficiency under the best conditions may be slightly lower than the case where the film did not go Cu-rich.

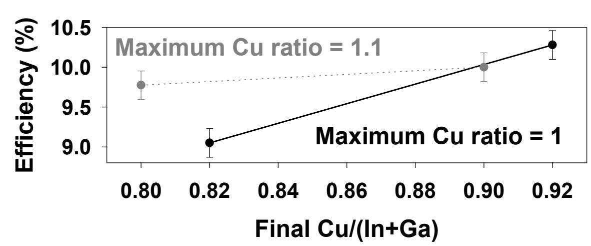
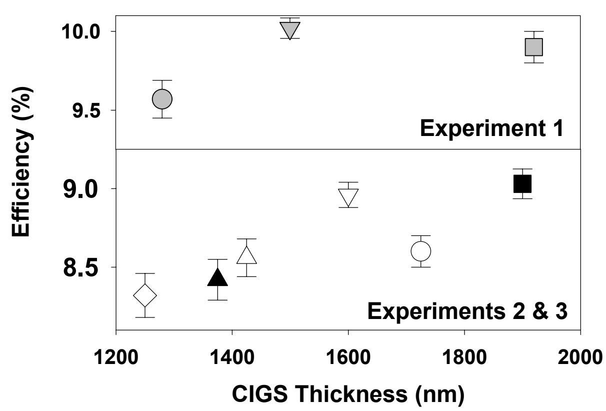


Figure 1: Interaction chart summarizing device efficiency from roll-coaters as a function of maximum and final Cu ratio.

As somewhat different conclusions were reached from the bell jar and roll-coater experiments, further examination of conditions in the roll-coater were performed. In these follow-up experiments, deposition temperature and film thickness (as varied either by source temperature or deposition time) were included as factors. Interpretation is more complex than for the earlier experiments, as – even for a constant maximum Cu ratio – thickness and resultant Ga profile impact performance. Substrate temperature is also a factor. These results are summarized in Figure 2, which shows efficiency as a function of the newly-introduced factors, for constant maximum Cu ratio. The legend lists the process conditions for each symbol. Analysis of the designed experiment and resulting error bars were generated using Statistica® software.

Thus, despite the demonstrated benefit of a Cu-rich growth period for bell jar devices, designed experiments performed in production roll-coaters determined that the effect of maximum Cu ratio is convoluted with film thickness, temperature, and time. Efforts are currently underway to fully optimize conditions and assign the inter-dependencies to physical mechanisms such as Ga profile.



Data Point	Web T	Source T	Web Speed	Max. Cu ratio	
● (grey circle)	High	High	High	Constant	Expt. 1
▼ (grey)	High	High	Medium	Constant	
■ (grey square)	High	High	Low	Constant	
▲	High	Low	Medium	Constant	Expt. 2
■	High	High	Medium	Constant	
○	Low	High	Medium	Constant	Expt. 3
▽	High	High	Medium	Constant	
◇	High	High	High	Constant	
△	Low	High	High	Constant	

Figure 2: Results from experimental design varying deposition temperature and CIGS thickness (by source temperature or web thickness) in roll-coaters, at constant Cu ratio .

3. POST-DEPOSITION TREATMENTS

Post-deposition treatments of production CIGS have been examined for a boost to efficiency and process robustness in two forms: surface sulfurization via thioacetamide and, post-deposition Na treatments following recent work by Rudmann et al.[1]

Over the past several years, two CIGS groups have reported relative device efficiency increases of as much as 20% due to an additional chemical treatment involving solutions containing thioacetamide.[2,3] The efficiency improvement is attributed to the formation of a thin sulfide layer and/or surface passivation by sulfur atoms. Thioacetamide treatments were evaluated on GSE production material by designed experiment. Treatment time, temperature, and concentrations were varied. Although optimum conditions were found to be consistent with those in the literature, no statistically significant performance benefit was realized compared to untreated samples. It was concluded that the benefit of the thioacetamide treatment is dependent either on some property of the CIGS surface not present in the GSE material, or on a procedural detail not reproduced in our experiments. Complete results will be presented at the upcoming IEEE PVSC meeting.

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[1] D. Rudmann, D. Bremaud, H. Zogg, A.N. Tiwari, "Na Incorporation for Low Temperature Cu(In,Ga)Se_2 Growth," *Proceedings of the 19th European PVSEC*, (2004).
[2] T. Nakada, K. Matsumoto and M. Okumura. "Improved Efficiency of Cu(In,Ga)Se_2 Thin Film Solar Cells by Surface Sulfurization Using Wet Process", Proc. of the 28th IEEE PVSC, (2002), p. 527.
[3] T. Wada, Y. Hashimoto, S. Nishiwaki, T. Satoh, S. Hayashi, T. Negami and H. Miyake. "High-efficiency CIGS Solar Cells with Modified CIGS Surface", Solar Energy Materials and Solar Cells, **67** (2001) p. 305.

Passivation of CIGS on flexible substrates by treatment with NaF has also been reported.[1] This work was applied in this study to production-line CIGS. At GSE, CIGS was deposited on 0.001" steel varying the deposition condition. The two types of material were subsequently sent to ITN for post-absorber treatment. Herein, a portion of each coupon set was treated with NaF and finished into devices, while another portion was finished into devices without post-absorber NaF treatment. Treatment time and temperature were examined as variables in the designed experiment. Optimum conditions were found to be consistent with those in the literature. Results for coupons 15 and 55, treated under the conditions reported by Rudmann, are shown by the blue bars in Figure 3. For both coupons sets – particularly for the lower efficiency material – the post-deposition Na passivation increases efficiency. GSE is investigating concepts to better implement and test passivation via NaF on the production scale level.

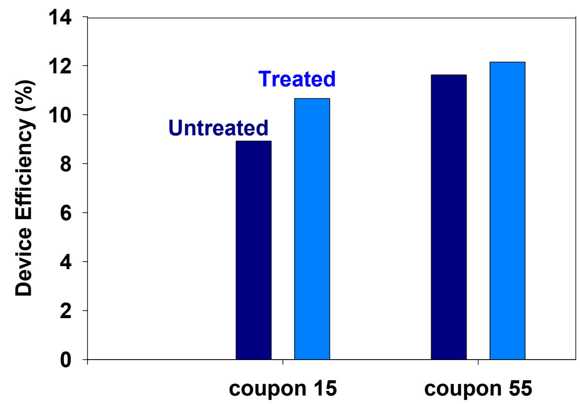

Figure 3: CIGS device efficiencies with and without exposure to post-deposition treatment.

4. SOURCE PURITY

Experiments examining the effect of metals source material purity on device properties were performed. Six CIGS films were made using three different source purities, resulting in 72 devices to be analyzed. Average open-circuit voltage at each source purity, after correction for small differences in Ga content between samples, is shown in Figure 4. It appears that open-circuit voltage decreases with source purity. Evaluation of other device parameters was not possible, as this sample set exhibited an inflection in the IV curve that is detrimental to short-circuit current and fill-factor. The latter attribute has been associated with thick or resistive window layers.[4,5,6] The examination is being repeated with a lower resistance i-ZnO, which has removed the inflection in the IV curve. The new films will allow examination over a larger sample set, as well as examination of all IV parameters. If the trend of increasing voltage with source purity continues to hold, an assessment of statistical

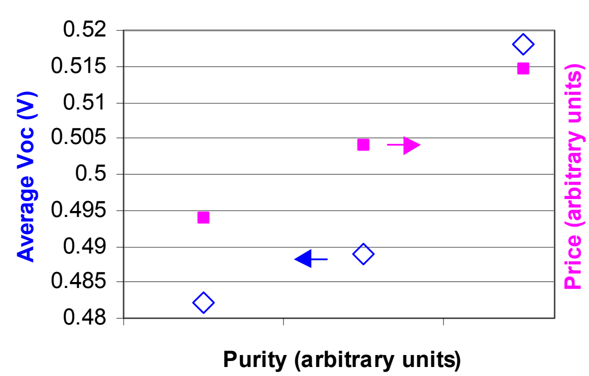

Figure 4: Open-circuit voltage and source material cost as a function of source material purity.

[4] T. Walter et al, Proc. 13th European PSEC, 1995, p. 1999.

[5] I.L. Eisgruber, J.E. Granata, J.R. Sites, J.Hou, J. Kessler, "Blue Photon Modification of Diode Barrier in $CuInSe_2$ Solar Cells", *Solar Energy Materials and Solar Cells*, **53**, pp. 367-377, 1998.

[6] M. Gloeckler, C.R. Jenkins, J.R. Sites, *MRS Proceedings*, **763**, 2003.

significance and the impact of specific impurities is likely to follow. This examination has direct implications for evaluating cost vs. performance trade-offs, as source material price increases with purity (right axis of Figure 4).

5. Deposition Time

Very fast deposition rates onto steel substrates, which simulate the high throughput in the production roll-coaters, are being implemented in the bell jar. Initial experiments indicate a possible sensitivity of device results to temperature ramp rate, which can be much faster for thin steel substrates than the typically-used higher thermal mass glass. Further analysis is underway.

6. Sensitivity to Substrate Properties

Use of aluminum oxide substrates in the bell jar is being examined for a route to information about the impact of Mo morphology and NaF optimization, independent of the roughness, impurity diffusion, and temperature control issues that can convolute results on steel. A considerable performance difference between CIGS deposited on different Mo morphologies on these substrates has been observed. SIMS data from Sally Asher and Matt Young at NREL confirms that the performance difference is not due to differing diffusion of Al or O from the substrate in the CIGS. Findings on this topic will be presented at the upcoming IEEE PVSC meeting. Further experiments, related to both NaF optimization and Mo morphology, are being planned.

7. Publications

A number of publications are in progress related to this contract. A paper describing the use of thermopile for endpoint detection in each stage of the three-stage process has been accepted to *Progress in Photovoltaics*, and proofs have been returned to the publisher:

- I.L. Repins, D. Fisher, W.K. Batchelor, L. Woods, M.E. Beck, "A Non-Contact Low-Cost Sensor for Improved Repeatability in Co-Evaporation of High-Quality CIGS", *Progress in Photovoltaics*, 2005, in press.

An overview of work done under this contract was presented at the recent Solar Energy Technologies meeting:

- J.S. Britt, M.E. Beck, I.L. Repins "Sensitivities in Roll-to-Roll Processing of CIGS-Based Photovoltaics on Flexible Metal Foils," *October 2004 SET Meeting.*

Drafts for three presentations (one oral, two posters) at the upcoming IEEE PVSC conference are being prepared:

- I.L. Repins, D.C. Fisher, M.E. Beck, "Effect of Maximum Cu Ratio during Three-Stage CIGS Growth Documented by Designed Experiment," *Accepted to January 2005 IEEE PVSC.*
- D.C. Fisher, I.L. Repins, W.K. Batchelor, J. Schaefer, M.E. Beck, "The Effect of Mo Morphology on the Performance of $Cu(In,Ga)Se_2$ Thin Films," *Accepted to January 2005 IEEE PVSC.*

- W. K. Batchelor, M.E. Beck, I.L. Repins, "Thioacetamide-Treated CIGS Solar Cells on Stainless Steel and the Effect on Device Performance," *Accepted to January 2005 IEEE PVSC.*

Best Wishes,

Markus E. Beck

Cc: Carolyn Lopez, NREL Subcontract Associate